PREPARATION OF BENZOIC ACID BY OXIDATION OF TOLUOL

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The Preparation of Benzoic Acid By Oxidation of Toluol

A THESIS

PRESENTED BY

D. W. GRIGSBY AND E. E. McCLUNG

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Object of Thesis.

The purpose of this investigation was to obtain a satisfactory yield of benzoic acid by the direct oxidation of toluene by chromic acid.

Many difficulties are met in carrying out this process, and the amount of acid produced is so small that up to the present time it is not successful commercially.

The difficulties appear to be largely mechanical, but it is quite possible that they may be chemical in nature.

The first intention of the writers in conducting this investigation was to vary certain mechanical features. This, because of certain unforeseen circumstances, was abandoned except to a limited extent. Attention was chiefly devoted to the study of the process as it has been attempted up to the present time.

A few preliminary tests showed that there was a great discrepancy between the amount of chromic acid reduced, and the amount of benzoic

acid produced. The purpose of the work carried out was to explain the discrepancy, and by the limited variations of conditions and apparatus possible, to attempt the production of satisfactory amounts of benzoic acid.

OXIDATION OF TOLUOL TO BENZOIC ACID.

Benzoic acid is an article of considerable commercial importance, being used in medicine, in the dye industry, in calico printing and as a preservative; also, certain of its esters are used as fruit essences and in perfumery. Its value was in 1918 from $2.50, to $2.75 per pound. It is a solid, crystallizing in either needle or leaf-like form, and possesses a characteristic odor. It melts at 120° C. and it may be distilled with steam. It is readily soluble in absolute alcohol, ether, carbon tetrachloride, carbon bisulphide, toluene, hot water, and, as will be mentioned later, in certain acid mixtures. It is only slightly soluble in cold water. Following is a table of solubilities in water: One thousand parts of water dissolve at,

0°	20°	40°	60°	80°	100°
1.7	2.9	5.55	11.55	27.15	58.75

parts of benzoic acid. (Thorpe)

Oxidation of Tolulol to Benzoic Acid.

The solubility curve of benzoic acid in water is, however, peculiar, since at 90° C. the benzoic acid melts below the water and there are consequently two layers composed of solutions of acid and water but of different concentrations. Above 116° C. only one layer exists since the acid dissolves more water, and the water more acid until at this temperature the layers are identical.

Benzoic acid occurs in many plants, and formerly the chief source was gum benzoin, from which it is obtained by sublimation. This is still the source of the acid which is to be used for medicinal purposes. The acid may also be obtained from hippuric acid. This method, which was the chief source of the acid production for the arts has been largely, or almost entirely abandoned in favor of toluene oxidation methods.

While the available literature on the subject of benzoic acid production is not exten-

sive, considerable work appears to have been done on the subject. There are German patents covering the separation of benzonitrile, C_6H_5CN, from the middle oils of coal tar distillation and the subsequent saponification to benzoic acid. The acid recovered is said to be very pure. Similar patents cover the similtaneous production of benzoic acid and phthalic acids from naphthols and other substitution products of naphthalene. This is accomplished by heating the above substances with fused alkalies and oxidizing agents. Blucher, (Industrial Chemistry) refers to the Ullman and Uzbachian process by which toluene is oxidized directly to benzoic acid by means of potassium permanganate. A 90% yield of pure acid is claimed. No other reference to this process was found, however, by the present writers.

From the numerous German patents issued it is evident that much work has been done with respect to the direct oxidation of toluene; for

instance, oxidation by ozone, using a catalytic agent. The most important method, and in fact, the method by which almost all benzoic acid is produced, is the formation of benzotrichloride by the direct chlorination of toluene and the subsequent decomposition of the latter by heating it with water under pressure; $C_6H_5CCl_3 + 2H_2O \rightarrow C_6H_5C$[illegible] $+ 3HCl$. However, all the benzoic acid prepared in this way is contaminated with chlor-benzoic acid, hence it is obvious that any successful method involving the direct oxidation of toluene is of advantage, and of commercial importance.

Theory

Chromic acid, CrO_3, when used as an oxidizing agent is reduced to Cr_2O_3, liberating three oxygen atoms. The reaction between chromic acid and toluene should be $C_6H_5CH_3 + 2CrO_3 = C_6H_5COOH + Cr_2O_3 + H_2O$. That is, one molecule of toluene is oxidized by two of chromic acid. The chief reason for the difficulty in oxidizing

toluene appears to be its lack of solubility in the oxidizing agent. To overcome this toluene is vaporized and is passed under pressure through the chromic acid which is contained in a lead-lined chamber. The temperature considered advisable is from 85- 90° C., and the pressure about two pounds. The benzoic acid produced remains dissolved in the chromic acid, but is removed by washing the latter with toluene. The solution resulting from the last operation is steam distilled; the toluene passes over leaving the benzoic acid dissolved in hot water from which it crystallizes out on cooling.

"Benzoic acid is quite stable in the presence of an oxidizing agent, and is not affected by dilute chromic acid. It is, however, attacked when warmed with H_2SO_4 and MnO_2, being converted into phthalic acid, formic acid, and CO_2." (Thorpe).

Chromic acid is soluble in water, and in concentrated sulphuric acid. When dissolved in

the latter it liberates oxygen. In sulphuric acid of I.77 sp. g. chromic acid is "said to be almost insoluble." The acid solutions used were prepared in the following manner: A known weight of CrO_3 was dissolved in a known amount of hot water; sulphuric acid was then added to the hot solution until the CrO_3 began to precipitate. An effort was made to obtain an acid solution of CrO_3, I9%; H_2SO_4, 40%; and water 4I% by weight. The amounts of water and CrO_3 were calculated on that basis.

The acid mixtures as used were analyzed by the following method: HCl in excess was added to a given weight of acid. $BaCl_2$ was added, precipitating barium sulphate. The H_2SO_4 was calculated from the $BaSO_4$. To the filtrate, containing the chromium as chromate were added a few c.c. of alcohol. It was then boiled until the odor of alcohol disappeared, when it has changed in color from orange to dark green. NH_4OH in slight excess was added, and the solu-

tion was boiled until all chromium was precipitated as $Cr(OH)_3$, leaving the supernatant liquid colorless. The $Cr(OH)_3$ was filtered through a Gooch crucible, ignited, and weighed as Cr_2O_3.

EXPERIMENTAL WORK PERFORMED

Several runs were first made with glass apparatus. Toluene was vaporized from a liter flask equipped with a mercury manometer. The toluene vapor was passed into a two liter flask, supported on a water bath, and containing a chromic-sulphuric acid mixture of approximately the following composition: CrO_3, 20%; H_2SO_4, 36%, and H_2O, 44% by weight. The toluene vapor was admitted thru a glass tube expanded at one end into a bulb about one and one half inches in diameter. The bulb which was below the surface of the acid mixture, was perforated with many small holes.

If the bulb is carefully annealed, the holes may readily be made by heating it and touching a hot platinum wire to the side. The wire is

quickly pulled away and a short tube is then drawn out from the side of the bulb. When this is broken off a hole of sufficiently small diameter is produced.

The flask, containing the acid mixture, was also connected to a condenser.

The toluene, in the liter flask, was heated to it's boiling point, III°C., and the vapor was passed thru suitable connections into the acid. A considerable quantity condensed before reaching the acid, and this, consequently, would not react with the acid. Considerable vapor passed over, however, as was evidenced by the violent bubbling of the vapor thru the acid. The bulb quite effectively accomplished its object of distributing the vapor thruout a considerable area. The manometer registered a pressure of from 2 to 4 inches of mercury, corresponding roughly to I to 2 pounds per square inch.

Oxidation of Toluol to Benzoic Acid

The temperature control was not carefully adjusted, and a higher temperature than was desired was obtained. The temperature of the water bath arose to 94° C., while that of the reacting substances was about 10° higher. When about two liters of toluene had passed thru, the operation being interrupted while more toluene was added to the vaporizing flask, the run was stopped. Considerable toluene which had passed from the acid containing flask thru the condenser was collected. It was, however, useless to attempt to make any accurate check upon the toluene used, and recovered, because of leakage, etc. during the operation.

The toluene remaining with the acid was syphoned off, and the acid was thoroughly washed three times with toluene. These washings were added to the first toluene removed, and the combined amounts were distilled with steam. The toluene distilled over, being at first colorless, but when nearly all removed it became yellow.

Oxidation of Toluol to Benzoic Acid.

Finally a watery, yellow liquid came over and intermingled with this were drops of a yellowish oil. This oil formed a distinct layer on top of the other liquid. At this stage no more toluene was coming over. The oil and the yellowish solution possessed an odor similar to that of nitro benzene. In only one run was the distillation carried on any farther than this. In the one run just mentioned, the liquid being distilled was divided into two equal parts just when the toluene had ceased coming over. One part was concentrated and cooled, and the benzoic acid crystallizing out was removed by filtration. The other portion was still further distilled with steam. In this latter case the distillate, after a time, became less colored, and the odor of benzoic acid was much in evidence. The distillation was discontinnued here, and the benzoic acid was separated from the remaining liquid in the same manner as in

the case of the other portion. All of the distillates were preserved.

The chromic acid had been partly reduced: $2CrO_3 \longrightarrow Cr_2O_3 + O_3$. The amount of reduction was determined in the following manner: To a few c.c. of acid was added an excess of standard ferrous ammonium sulphate. The color of the acid, which had been previously been diluted with water to 50 c.c., turned a dark grass-green. The excess of the ferrous ammonium sulphate was titrated with standard $\frac{N}{10}$ $KMnO_4$. The end point is the appearance of a pinkish tinge which is observed in the green solution. At the end point the solution suddenly darkens. The amount of CrO_3 present is calculated from the amount of ferrous ammonium sulphate reduced. $ICrO_3 = 3FeSO_4(NH_4)_2\ SO_4.6H_2O$. This analysis showed a complete reduction of the chromic acid solution. Nevertheless, the amount of benzoic acid recovered was very small, entirely out of proportion to the theoretical amount.

Oxidation of Toluol to Benzoic acid

All of the reduced acid was saved for subsequent work. Incidentally it should be mentioned that the reduced acid solution can be electrolytically reoxidized to chromic acid.

For the purpose of obtaining better temperature and pressure control, and of using apparatus similar to that which would be used industrially, a different type of oxidizing chamber was used.

This chamber consisted of a rectangular lead box I0 inches long, 8 wide, and 6 inches deep. The lead was I/8 inch thick, and was bent outward at the top, forming a horizontal surface I/2 inch wide, and extending entirely around the box. A pyrex baking dish of transparent glass was used as a cover. A I/2 inch lead pipe entered the box 2-I/2 inches from the top, but it was bent downward to within I/2 inch of the bottom and then around the sides of the box one-half inch from the bottom, and one-half inch from the

walls. The end of the pipe was sealed, and at the point of entrance the pipe was made an integral part of the box by burning. Numerous small holes were punched in the pipe along its inner surface. Several holes were drilled in the box. One, I-I/2 inches from the top, near a corner of the box on the side opposite that through which the pipe entered, was used to admit a I/2 inch glass tube. This glass tube was connected to a condenser, a valve being inserted in the connection. A mercury manometer was inserted through another hole, likewise, I-I/2 inches from the top, and by boring a hole diagonally through a side of the box, it was possible to insert a thermometer so that it extended nearly to the bottom, and yet the hole would not be below the surface of the acid in the box. All the holes were made leak proof by using a mixture of asbestos, $BaSO_4$, and water-glass.

The distilling vessel for toluene consisted

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of a copper vessel with a cap from which extended, at right angles, a short tube. This tube was inserted in the lead pipe extending into the box, and the joint was sealed with the above mentioned mixture. The cap was not a screw cap, but was fastened by a clamp. No convenient gasket was available, and it was found later that there was considerable leakage of toluene at this place. This would have been the most suitable pointfor a pressure gauge, but it was not found convenient to insert one.

In making the runs, a measured amount of acid was placed in the box, and the box was then supported on a water bath. The cover was placed on the box and all cracks were stopped with the $BaSO_4$, asbestos water-glass mixture. The cover was held in place by suitable clamps. The temperature in the box was raised to 85° C., and then the toluene was heated. The toluene vapor then passed over into the acid mixture. The valve between the box and condenser was closed.

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In the first run the toluene came through quite vigorously, but the distribution was not what was desired. Most of the vapor escaped through the first few holes. In the second run this was corrected by sealing these holes with water-glass. In this latter run the distribution was very satisfactory. Considerable toluene vapor was observed above the acid surface. But little pressure was indicated by the manometer. This, of course, did not register the actual pressure of the toluene which was forced through several inches of acid. In the second run a pressure of one inch of mercury was registered by the manometer. In no case did the temperature exceed 90°.

After the runs were completed the same methods of benzoic acid extraction were followed and the same analyses were made as have already been described in the case of the preliminary runs.

It was observed that the acid mixtures which

had been used in the oxidation became partly solid after standing some days. The solid portions did not give the appearance of pure chromic salts, consequently much attention was devoted to tests on the acid to determine whether, or not, the benzoic acid had been entirely removed by washing with toluene. It was farther noticed that when benzoic acid was dissolved in hot dilute, H_2SO_4, it crystallized out on cooling. When, however, some of the chromic acid mixture was added, and the benzoic acid brought into solution, it remained in solution when cooled.

Since benzoic acid distills in steam, a steam distillation was conducted on the chromic acid. No trace of benzoic acid was found in the distillate. Various solutions were used in the attempt to extract the acid. Small amounts of the various washings were evaporated from watch glasses. Traces of benzoic acid were left by all of the solvents used. Among the solvents used were CS_2, alcohol,

ether, CCl_4, toluene, etc. The CS_2 appeared to be the most effective. Nevertheless, the tests indicate that there is no considerable amount of benzoic acid left in the chromic acid.

Alcohol and ether acted differently than the other solvents. After these two had evaporated from the watch glass, a yellowish oil was left with the white benzoic residue, and when the liquid had been completely evaporated the residue emitted a strong acetate odor.

It has been mentioned that in the steam distillation a cut was obtained in the distillate consisting of a yellowish watery liquid and lighter yellow oil. It was first assumed that the color was due to a chromium compound that might have been carried over. This was found not to be the case. When alcohol was added to a portion, and the mixture was boiled, no change of color from yellow to green was produced. When the odor of alcohol had been removed by boiling, NH_4OH was added, and

the solution was kept at the boiling point for a few minutes. A flocculent precipitate appeared, and the liquid turned reddish brown. The precipitate was filtered off and ignited. It proved to be organic in nature. A part of the yellow liquid was raised to its boiling point. It was found to boil at 102° C., with no change after some minutes of boiling. It possessed a disagreeable odor, similar to that of nitrobenzene, and irritated the eyes. Needless to state, no contamination with the latter substance was possible.

The toluene used had been washed with H_2SO_4, so that contamination with 2 and 3 - methylthiophene was not possible. Coal tar toluene, not subjected to this washing, is always so contaminated.

The tests performed, and the purity of the reagents, indicate that the yellow product is produced during the oxidation, and might be an

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important factor in the lack of success of the process.

DATA AND CALCULATIONS

Standard Solutions:

Ferrous ammonium sulphate 1 c.c. contains .02513 gm. $FeSO_4$.

Potassium permanganate 1 cc. = 1.405 c.c. $FeSO_4$ $(NH)_4$ SO_4 sol.

Acid used: Analysis:

CrO_3	500 gm.	25.3%
H_2O	917 "	46.73%
H_2SO_4	729 "	33.97%

Gravimetric analysis: 1 c.c. acid = .2543 gm. CrO_3.

Bom run I.

Acid used .....2 liters

Toluene used, including washings. 5,750 c.c.

Toluene recovered, " " .. 3,688 c.c.

Toluene consumed ..... 62 c.c.

Weight of benzoic acid recovered. 2.49 gm.

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Final acid analysis, 1 c.c. contains.. .1571 gm.
unreduced CrO_3.
CrO_3 used per c.c. - .2543 - .1571 = .0972 gm.
Total CrO used, .0972 X 2000.....199.4 "
Theoretical yield of benzoic acid based
on toluene consumption.....70.77gm.
Theoretical yield based on toluene con-
sumption CrO_3 ..... 118.65.
Box run II:
Acid used, 2 liters.
Toluene used, including washings.... 3000 c.c.
Toluene recovered, " " .... 2850 "
Toluene consumed ..... 150 c.c.
Weight of benzoic acid recovered.... 5.97 gm.
Final acid analysis, 1 c.c. = .1529 gm. CrO_3.
CrO_3 used per c.c. - .2543 - 1529 ... .1014.
Total CrO_3 used, ... 202.8 gm.
Theoretical yield of benzoic acid based
on toluene consumption..... 171.27.
Theoretical yield CrO_3 based on toluene
consumption..... 123.8

Oxidation of Toluol to Benzoic Acid

sample calculations:

Toluene, molecular weight, 92.1; Sp.g... .8614

Run I, 65 c.c. used, 62 x .8614 = 53.39 gm. used.

1 toluene = 1 benzoic acid.

The molecular weight of toluene divided by the amount of toluene used equals the molecular weight of benzoic acid divided by the amount of benzoic acid produced.

$$\frac{92.1}{122.09} = \frac{53.39}{x}\ ;\quad x = 70.77 \text{ gm.}$$

2 CrO_3 = 1 benzoic acid,

$$\frac{200}{152.09} = \frac{194.4}{x};\quad x = 118.65 \text{ gm.}$$

benzoic acid.

SUMMARY

In the conduct of work described, it was found that many unexplained difficulties presented themselves, and several of these might be profitably investigated.

With laboratory apparatus, and the limited means of operation available, the production of benzoic acid by this method is not a success, since the yield is only about five percent of the the-

oretical amount based on the reduction of the chromic acid.

The percentage yield of the second bom run was about twice that of the first. This, it was concluded, was due to the fact that a greater pressure was used, and the vaporization of toluene was more effective. That is, the vapor was kept constantly flowing, and at a rapid rate. The distribution of the vapor through-out the acid was, likewise, much better. Another difference, which might have had some influence, was that in the second case no time was allowed to elapse between the end of the run and the extraction of the benzoic acid. The loss of toluene by leakage was greater in the second run, however, than in the first.

Had time permitted, an effort would have been made to confirm the conclusion reached, that oxidation products, other than benzoic acid are formed, and to determime, if possible, what the

products are. Also, the possibility of the formation of sulphonic acids would have been investigated.

An effort would, likewise, have been made to devise apparatus by which the toluene could be constantly drawn off, and not allowed to accumulate in the oxidizing chamber. The method of vaporizing, and the distribution of the vapor, are matters of mechanical detail, to which considerable attention should be given.

Finally, it seems certain that no successful production of benzoic acid can be obtained with apparatus similar to that used. But, nevertheless, it appears quite probable that by modifying conditions and apparatus, the process might be made a success.